X-Ray Structural Investigations of Gold Compounds

A COMPILATION OF REFERENCE DATA. PART II

Peter G. Jones
Inorganic Chemistry Institute, University of Göttingen, Federal Republic of Germany

VII. Square Planar Gold(III) Complexes

The archetypal coordination geometry of Au^{III} was established in several early, and necessarily somewhat inaccurate, studies. Thus, $KAuBr_4.2H_2O$ was shown in 1936 to contain square planar $AuBr_4^-$ ions (98), $(n\text{-}C_3H_7)_2AuCN$ to consist of square tetramers with bridging CN groups (99), Et_2AuBr to be dimeric with bridging Br (100) and Me_3PAuBr_3 to be monomeric, again with square planar coordination at Au (101).

AuX_4^- and Related Species

A large number of $AuCl_4^-$ salts has been studied (Table VIa), although this ion was not always the main object of interest; it often occurs as a stabilizing 'large anion'. The Au-Cl distances are rather variable, an average of 24 of the more accurate values reported being 227(1) pm.

More examples of AuX_4^- and related species are given in Table VIb and in Section IX. In all cases the

Table VI

(a) Bond Lengths in Some $AuCl_4^-$ Salts

Cation	Au-Cl bond length, pm	Comments	Reference
K^+	220-237 (2)	Pseudosymmetric	102
Na^+	226.0(.6),227.8(.6),228.3(.6),228.8(.5)	m^*	103
Rb^+	227.8(.7),228.6(.8)	$\bar{1}^*$	103a
NH_4^+	225.3(1.2),225.4(.8),226.4(.8), 227.4(.9),228.1(.7),228.3(.8)	2^{**}	104
NH_4^+	218-229	$Ag_2Cl_5^{3-}$ ions present	105
$(pyridine)H^+$	227.0(.2)	$2/m^*$	37b
Ph_4As^+	227.1(.4)	4^*	106
hypoxanthinium	228.7(.6),229.2(.6),227.5(.6),227.7(.6)		107
S-benzyl-isothiouronium	226,226,226,228(2)		108
$(dimethylacetamide)_2H^+$	225.8(.7),227.2(.6)	$\bar{1}^*$ X-ray diffraction	
	226.6(.3),226.3(.3)	Neutron diffraction	109
$(Ph_3PO)_2H^+$	226.9(.5),228.0(.6)	2^*	110
$H_5O_2^+$		Neutron diffraction; disordered	111 nc

(b) Bond Lengths in Further AuX_4^- (and Related) Salts

Compound	Au-X bond length, pm	Comments	Reference
$KAuF_4$	195(2)	$4/m^*$; neutron diffraction	112
$RbAuBr_4$	241.7,243.4†	$\bar{1}^*$	113
$HAu(CN)_4.2H_2O$	195,199(2)	$\bar{1}^*$; contains $H_5O_2^+$	114
$KAu(CN)_4.H_2O$	av.198(1)	Neutron diffraction, repeat of earlier x-ray study (116)	115
$KAuCl_2(CN)_2.H_2O$		Low accuracy	117
$KAu(NO_3)_4$	199(1),202(2)	$\bar{1}^*$; unidentate NO_3^-	118
$[Ph_4As][Au(-C{=}N\text{-}N{=}N\text{-}N(C_3H_7))_4]$	195-200(4)		119
$[(NH_3)_4Au](NO_3)_3$	202(1)	mmm^*	120

*Au on special position with this symmetry
**Two independent Au, one on special position with this symmetry
†Calculated from published coordinates

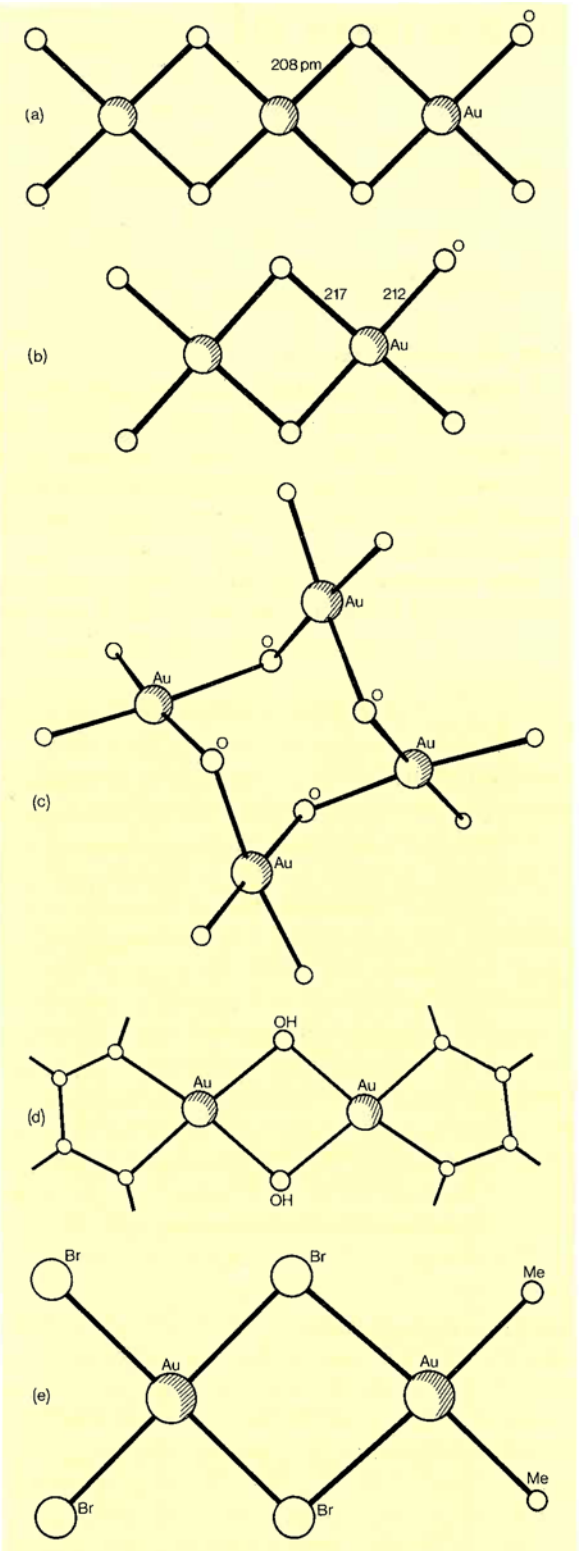

Fig. 24 Some oligo- and polymeric Au^{III} structures.
(a) part of the infinite $(AuO_2^-)_n$ chain in $KAuO_2$. After (122)
(b) the dimeric $Au_2O_6^{6-}$ ion in 'Na_3AuO_3'. After (123)
(c) the tetramer $[Me_2AuOH]_4$. After (124)
(d) the auracyclopentadiene dimer, in which the phenyl rings are omitted for clarity. After (125)
(e) the dimeric $[MeAuBr_2]_2$. After (130)

geometry is square planar, although the formal crystallographic symmetry may be less than the ideal *4/mmm*. Strähle has studied symmetry relationships among halide complexes; thus, $RbAuBr_4$ (113) is virtually isostructural with $RbAuCl_4$ (103a), though of formally lower symmetry. Similarly, $LiAuCl_4.2H_2O$ is in space group *P4/mmm*, the corresponding Br and I salts being in a closely related cell of lower symmetry (*A2/a*). These latter compounds can be converted into *P4/mmm* forms on heating (121).

Other Au^{III} compounds will be grouped for discussion according to ligand (as for Au^{I} above; see also Section I).

Compounds with Oxygen Ligands

The compounds Li_5AuO_4, $KAuO_2$ and $RbAuO_2$ have been shown from powder data to contain infinite chains of the form shown in Figure 24 with the Au-O bond lengths about 208 pm; Li_3AuO_3, however, contains discrete $Au_2O_6^{6-}$ ions (122). A single crystal study of $Na_6Au_2O_6$ (123) confirms the presence in this compound of these ions (Figure 24) which are isoelectronic with the binary gold halides Au_2X_6. Au-O bond lengths are 212 pm (terminal) and 217 pm (bridging). These are appreciably longer than in Au_2O_3 (2), possibly because of additional Na...O interactions.

The hydroxide complexes Me_2AuOH (124) and 1-hydroxy-2,3,4,5-tetraphenylauracyclopentadiene (125) have been shown to be tetrameric and dimeric respectively (Figure 24), although in both cases the structure determinations were not of sufficient accuracy to provide reliable bond lengths. The only aquo-complex which has been reported upon is $Me_2Au(H_2O)(CF_3SO_3)$, with Au-OH_2 = 215.7(.6) pm and Au-OSO_2CF_3 = 220.1(.6) pm (126). This compound is extraordinarily difficult to obtain in anhydrous form. It possesses internal hydrogen bonds, which are probably responsible for the exactly planar Au-O-S-C-F moiety.

Compounds with Nitrogen Ligands

Few Au^{III}-nitrogen complexes have been structurally characterized, and those structures which are available are not always straightforward. Thus, $[Au(py)_2Cl_2]Cl.H_2O$ is both twinned and pseudosymmetric, and weakly coordinated by a further Cl^- and H_2O to give a highly distorted octahedral environment at Au (37b). (Further examples of distorted higher coordination number compounds, often with N ligands, are given in the next section.) The structure of (4,4'-azotoluene)$AuCl_3$ shows a disordered N-N group (127). Although (py)$AuCl_3$ has been studied, no details are available (37a nc, 37b nc). This leaves only four fully determined Au^{III}-N structures. Of these, that of $(NH_3)AuCl_3$, obtained by thermal decomposition of NH_4AuCl_4, shows no unusual

Table VII

Bond Lengths in Some Organogold (III) Derivatives

Compound	Au-C bond length, pm	Comments	Reference
$Me_2Au(H_2O)(CF_3SO_3)$	201.7(.8),201.9(.9)	At -160°C; *m**	126
$[Me_2AuOH]_4$	205(8)av.	Low accuracy	124
$[MeAuBr_2]_2$	212 (1)	at -160°C; *2**	130
cis - $[(Me_3PAuMe_2)(CF_3)C=C(CF_3)(AuPMe_3)]$	211,214 to Me, 203 to C.CF_3	Mixed valence; no e.s.d.'s	74a nc
$Br_3Au(o\text{-}Ph_2P.C_6H_4.Ch=CH_2)$†	210(3)		131 nc
$Br_3Au(o\text{-}Ph_2P.C_6H_4.CH_2Ch=CH_2)$	213(4)		131 nc
cis-$Ph_3PAu(C_6F_5)_2Cl$	218(10) trans to P, 212(9) trans to Cl		133 nc
cis-$PhAuCl_2(S\text{-}nPr_2)$	200(1)		132 nc
Aura-cyclopentadiene dimer**	205 av.	Low accuracy; $\bar{1}$‡	125
$Me_3AuCH_2SOMe_2$	214,211,216(5) to Me, 214(5) to CH_2		134 nc
$Me_2Au((CH_2PMe_2)_2BH_2)$	211.9(2.2),210.4(2.4) to Me, 215.9(2.2),217.4(2.1) to CH_2		136
$Me_2Au((Ch_2PMe_2)_2CH)$§	209.8(1.8),208.1(1.6) to Me, 214.7(1.6),211.3(1.5) to CH_2		135
$Me_2Au((CH_2PMe_2)_2N)$	208.7(2.2),210.4(2.1) to Me, 215.4(1.9),211.7(1.9) to CH_2		135
trans-$[((p\text{-}MeC_6H_4NH)_2C)_2AuI_2]^+ ClO_4^-$	207(2),209(2)		137 nc

* Au atom on special position with this symmetry
** See Figure 24
† See Figure 25 for chemical structure
‡ Two independent Au atoms on special positions with this symmetry
§ See Figure 26

features (Au-N = 201.2(1.5) pm) (57). In the ion *cis*-$[Au(SO_3)_2(NH_2CH_2CH_2NH_2)]^-$ the Au-N bonds are appreciably longer, 211.9 and 213.3(.7) pm, perhaps owing to the influence of Au-S bonds in *trans* position to them. A comparison of the tris-amine complex $[(NH_2CH_2CH_2)_2NHAuCl]^{2+}$ and the related amide $[(NH_2CH_2CH_2)_2NAuCl]^+$ (129) shows some significant differences; the Au-Cl bond of the amide is some 6 pm longer, which is attributed to a greater *trans* effect from N^- than from NH, and its coordination geometry is tetrahedrally distorted. The Au-N bond lengths show no clear pattern, being 197, 205 and 198(2) pm in the amine, and 205, 206 and 201 pm in the amide.

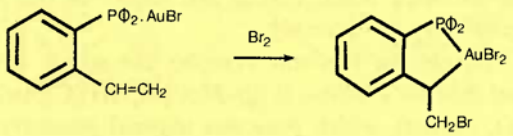

Fig. 25 The unusual bromination reaction of Au^I complexes of unsaturated phosphines, as proved by the X-ray structure of the product. After (131)

Organogold(III) Derivatives

As in the case of Au^I, a considerable variety of organometallic derivatives of Au^{III} is known. Again, the problem of locating light C atoms in the presence of gold leads to relatively inaccurate bond length determinations (Table VII), and generalizations relating Au-C bond lengths to probable electronic structures are difficult to make. However, important chemical information is often provided by the literature, even in the absence of accurate bond lengths. Thus, the $MeAuBr_2$ dimer has been shown to possess the 'unsymmetric' structure (Figure 24) (130). The bromination of Au^I complexes of olefinic phosphines leads not to the obvious products, but to the formation of C-Au and C-Br bonds as shown in Figure 25 (131nc).

The *trans* effect has been observed in the organogold(III) complex *cis*-$PhAuCl_2(S\text{-}nPr_2)$, the Au-Cl bond *trans* to Ph being appreciably longer than that *trans* to S (238 against 227(1) pm) (132nc). A similarly long Au-Cl bond (238(2) pm) is observed *trans* to C_6F_5 in *cis*-$Ph_3PAu(C_6F_5)_2Cl$ (133nc). Surprisingly, of the two bromogold complexes above, only one shows a marked *trans* effect in its Au-Br bonds (246, 251(1) pm), while in the other they are equal (249(1) pm) (131nc).

In recent years, several ylid complexes of Au^{III} have been prepared. The sulphoxonium ylid complex $Me_3AuCH_2SOMe_2$ was characterized by X-ray structure determination (134nc). A series of isoelectronic

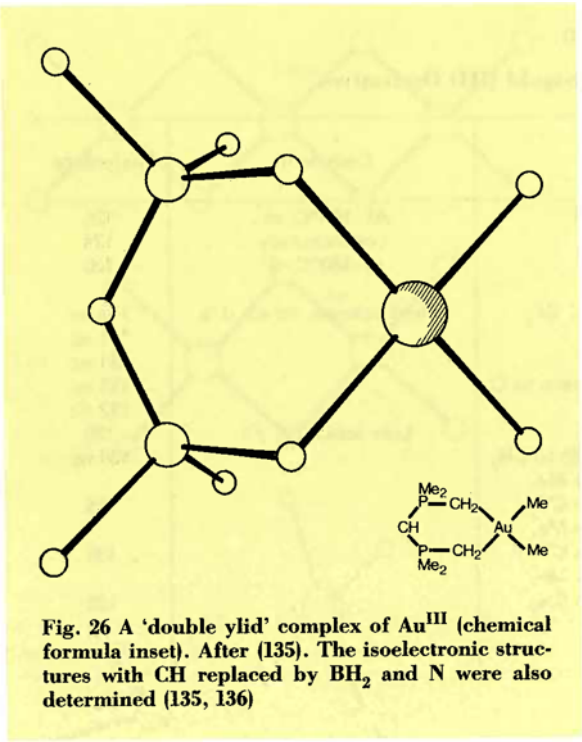

Fig. 26 A 'double ylid' complex of Au^{III} (chemical formula inset). After (135). The isoelectronic structures with CH replaced by BH_2 and N were also determined (135, 136)

double ylid complexes (Figure 26) has been studied by Schmidbaur and his co-workers (135, 136); these compounds show essentially identical coordination at Au, although bond lengths and angles of the ylid ligands vary considerably.

The sole Au^{III}-carbene complex for which structural data are available is $[((p\text{-}MeC_6H_4NH)_2C)_2AuI_2]^+ ClO_4^-$ (137nc), which possesses trigonal geometry at the carbenoid C atoms.

As already stated, generalizations about Au^{III}-C bond data are barely justifiable, in view of their low accuracy; the average bond lengths are as follows: Au-sp^3C (average of 14) = 210(4) pm, Au-sp^2C (average of 7) = 207(4) pm, Au-ylid C (average of 7) = 214(2) pm. The differences are scarcely significant, although the longer Au-C and short P-C bonds involving ylidic carbons may indicate some residual ylidic characteristics in the ligands even after complexing.

Complexes with Phosphorus or Sulphur Ligands

Several complexes of Au^{III} with phosphorus, where the chief interest lay in the other ligands, have been described already. Only Ph_3PAuCl_3 (138) remains to be mentioned; it shows a substantial difference in Au-Cl lengths, the bond *trans* to P being 234.7(.4) pm in length, the others 227.3 and 228.2(.4) pm.

Amongst sulphur complexes, thianthrenegold(III) chloride has been shown to be monomeric, only one of the two S atoms of the ligand being coordinated to Au (139). Also rather disappointingly, the dithiolate complex '$[Ph_3PAu(S(CF_3)C=C(CF_3)S)_2]^+Cl^-$' was shown to be $[Ph_3PCl]^+[Au(S(CF_3)C=C(CF_3)S)_2]^-$ and thus not five-coordinate (140). A series of complexes of the bidentate ligands di-*n*-butyldithiocarbamate ($Bu_2NCS_2^-$, 'dtc') and maleonitriledithiolate (*cis*-$S(CN)C=C(CN)S^{2-}$, 'mnt') has been investigated by Dutch workers. The structures of these compounds confirm the extremely strong tendency of Au^{III} to square planar coordination, even when the empirical formulae might suggest otherwise. The main deviations from ideal geometry are due to the small 'bite' (S...S distance) of the dtc ligand; typical S-Au-S angles for dtc are about 75°. The Au-S bonds are slightly longer for dtc, averaging 233(1) pm against 230(1) pm for mnt in complexes containing only these S ligands; it has been suggested that the weaker bonding is due to poorer orbital overlap at the narrow S-Au-S angle. The compounds reported upon were: $[Au(dtc)_2]^+[Au(mnt)_2]^-$ (141); the isomeric (dtc)Au(mnt) (142); $[Au(dtc)_2]^+Br^-$, with non-coordinated bromide ions (143); $[Au(dtc)_2]^+[AgBr_2]^-$, which is not isostructural with the analogous $AuBr_2^-$ compound (see Section IX) (144); $Au(dtc)_3$, with one bidentate and two monodentate dtc ligands (145); $Br_2Au(dtc)$, solved only in projection but shown to be isostructural with the Cu^{III} analogue (146nc); $Cu_2Au(dtc)_6Hg_2Br_6$, containing disordered Cu^{III}/Au^{III} sites (147); and $Br_2Au(dtc).\frac{1}{2}$(olefin), in which there are no interactions between the gold complex and the olefin (olefin = *trans*-stilbene or *trans*, *trans*-1,4-diphenyl-1,3-butadiene) (148).

VIII. Gold(III) Complexes with Higher Coordination Number

In square planar complexes the axial sites are, by definition, unoccupied by ligands. However, efficiency of packing in the crystal may dictate that some species should lie along these axes, even if rather distant from the gold atom. Such contacts to the gold atom are often too short to be purely non-bonding, and the coordination geometry may be described as highly distorted octahedral. Many of the Au^{III} complexes already described show such features, for instance $[Au(py)_2Cl_2]Cl.H_2O$ (37b), with Au...Cl = 317 pm and Au...O = 305 pm. Where to draw the line between 'packing' contacts and 'genuine' weak bonding is clearly a subjective decision. The addition compound between $H_3O^+AuCl_4^-$ and 2,2-dimethyl-2*H*-benzimidazole-1,3-dioxide shows axial Au...O contacts of 318 pm (Au-O bonds in Au^{III} oxide complexes are about 210 pm) and has been described as 'approximately octahedral' (149) while $[Au(diars)_2I_2]I$ has been reported as 'octahedral' (150). In this latter case the Au...I contacts — 335(2) pm or some 75 pm longer than a 'real' Au^{III}-I bond (137) — may be regarded as weak, but genuine, bonds.

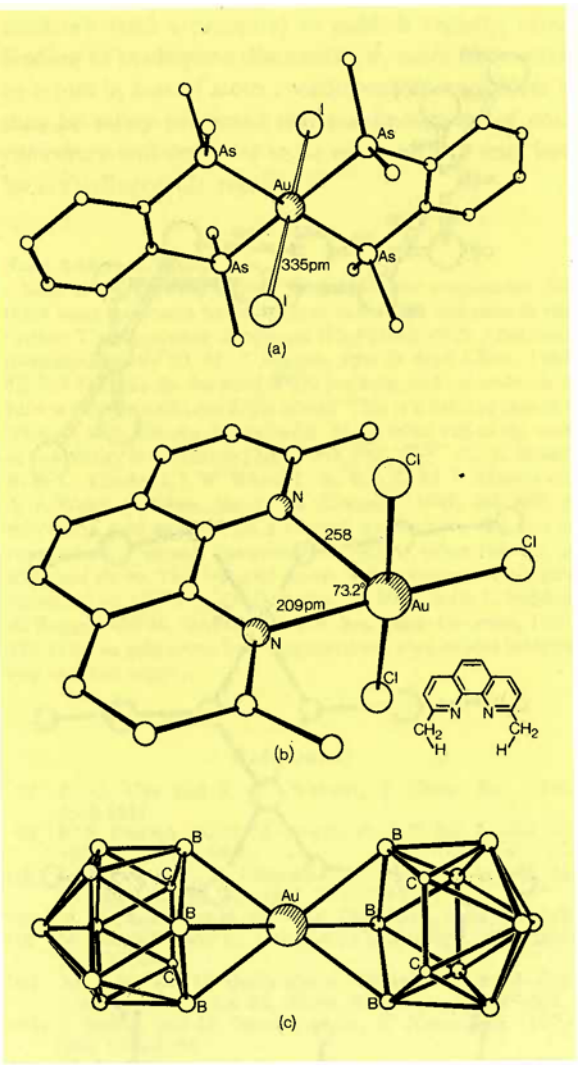

Fig. 27 Some examples of higher coordination number in Au^{III} complexes.
(a) $[Au(diars)_2I_2]^+$. After (150)
(b) trichloro-(2,9-dimethyl-1,10-phenanthroline)gold(III) and (inset) the chemical formula of the ligand, showing the H atoms which prevent more regular coordination. After (153)
(c) the carbaborane derivative $[(B_9C_2H_{11})_2Au]^-$. After (157)

More obvious cases of increased coordination number involve chelating ligands. The ligand $\alpha,\beta,\gamma,\delta$-tetraphenylporphinate (TPP) is ideally suited to square planar coordination, and the complex (TPP)$Au^{III}Cl$ adopts square pyramidal geometry with a long axial Au-Cl bond of length 301 pm (151nc). Other cases of five-coordination involve bidentate nitrogen ligands L and are of general formula $LAuX_3$ (X = halide). The ligands L possess H atoms so placed as to impede the coordination of a further two atoms in the square plane containing the Au and N atoms (Figure 27). Thus, regular square planar (and regular square pyramidal) geometry is ruled out. For L = 2,2′-biquinolyl and X = Cl (152nc), the $AuCl_3$ moiety and one N atom lie in a plane, but the second N atom cannot adopt the ideal axial position because the 'bite' of the ligand is too small. The bond lengths are irregular, but there are no very long bonds; Au-N = 228 and 240 pm, Au-Cl = 219 (*trans* to N), 235 and 238 pm. An alternative description based on a trigonal bipyramid is also unsuitable; two Cl atoms can be regarded as axial, but one Cl is displaced by 74 pm from an ideal equatorial site. As with most irregular five-coordinate systems, the geometry can be described either as distorted square pyramidal or distorted trigonal bipyramidal. For L = 2,9-dimethyl-1,10-phenanthroline and X = Cl or Br (153), the main features — Au, 3X and one N approximately coplanar, the second N displaced from the axial position — are the same as in the previous example. In contrast, however, the Au-X bond lengths are almost equal (226.7 to 228.5, 239.8 to 241.9 pm for X = Cl, Br respectively), the equatorial Au-N bond is shorter (208, 209(1) pm) and the axial Au-N longer (258(1), 261(2) pm). These features make the distorted square pyramidal description more applicable. Similar structures are observed for L = 2-(2′-pyridyl)-quinoline and X = Cl or Br (154); however, the axial Au-N bonds are somewhat longer (268, 264(2) pm). In all these cases five-coordination has been forced, in that the coordination of one N atom automatically brings the second within bonding distance, which is a situation similar to that observed for some Au^I complexes (see Section VI).

Finally, two complexes of the carbaborane anion $B_9C_2H_{11}^{2-}$, both having the empirical formula $(Et_2NCS_2)Au(B_9C_2H_{11})$, have been characterized as the monomer (155nc, 156) and ionic dimer $[(Et_2NCS_2)_2Au]^+[(B_9C_2H_{11})_2Au]^-$ (155nc, 157) respectively. In both cases the Au atom is bonded to all three B atoms of the open C_2B_3 ligand face, with Au-B = 220(1), 221(2) and 223(2) pm (monomer) or 220.4(1.1), 225.4(.9) and 227.3(1.0) pm (all twice, dimer). This implies five- and six-coordination in the monomer and dimer respectively.

Figure 27 shows some examples of higher coordination number for Au^{III}.

IX. Mixed Au(I)/Au(III) Species

It was recognized, thanks to some early crystal structure determinations, that several apparent derivatives of Au^{II} in fact consist of equimolar Au^I and Au^{III} components. Thus, '$CsAuCl_3$' is really $Cs_2(Au^ICl_2)(Au^{III}Cl_4)$ (158), '$(C_6H_5CH_2)_2SAuCl_2$' is a (disordered) mixture of LAuCl and $LAuCl_3$ (159), and 'DMGAuCl' (DMG = dimethylglyoximate) is $[(DMG)_2Au]^+[AuCl_2]^-$, in which only the Au atoms

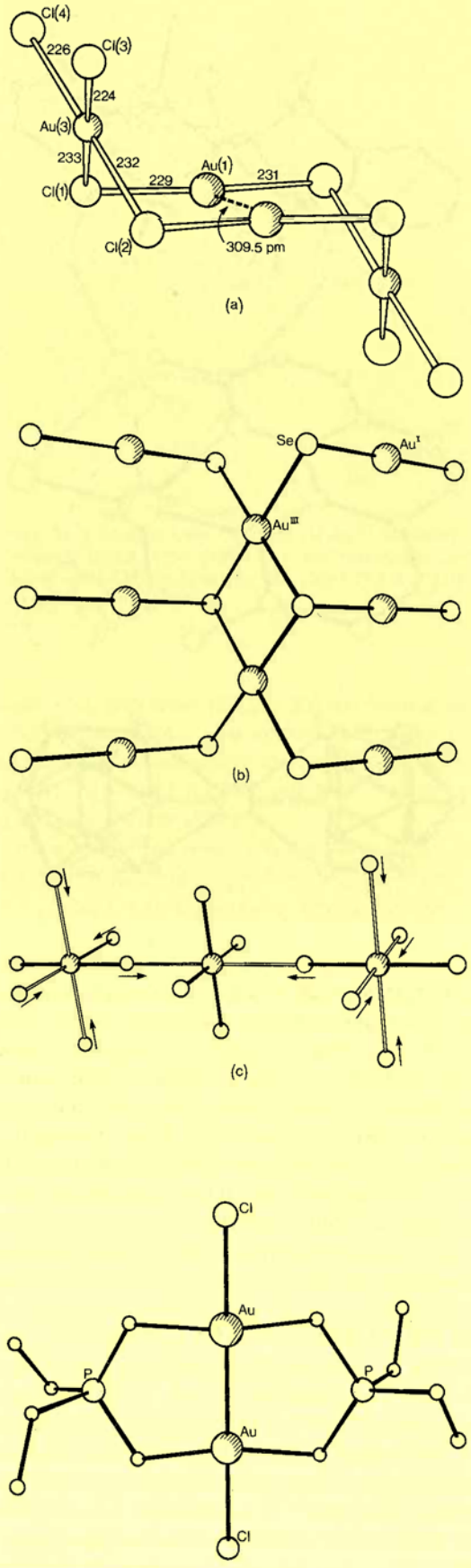

Fig. 28 Mixed Au^{I}/Au^{III} species.
(a) Au_4Cl_8, reproduced from (49) with permission
(b) part of the β-AuSe polymer. After (4)
(c) $Cs_2Au_2Cl_6$ at 1 atm. pressure, open bonds indicating weak Au...Cl interactions. With increasing pressure, the Cl atoms move in the directions shown by the arrows, thus tending to equalize the Au-Cl and Au...Cl distances. After (61)

were located (59). More recent work has confirmed similar constitutions for '$AuCl_2$' (really $Au^{I}_2Au^{III}_2Cl_8$, see Section IV and Figure 28) (49nc), 'AuSe' ($Au^{I}Au^{III}Se_2$, see Section I and Figure 28) (4), and '(dtc)$AuBr_2$' $[(Au(dtc)_2]^+[AuBr_2]^-$, see Section VII) (160). Two more complicated examples are *cis*-$[(Me_3PAu^{III}Me_2)(CF_3)C=C(CF_3)(Au^{I}PMe_3)]$ (74a nc) and $K_5Au_5(CN)_{10}I_2.2H_2O$, now revealed to be $5K^+.[Au^{I}(CN)_2]^-_4[Au^{III}(CN)_2I_2]^-.2H_2O$ (161).

The structure of $Cs_2Au_2Cl_6$ has been re-determined (61) to iron out some inaccuracies of the earlier determination, and also investigated at high pressure (162). At room temperature there are additional weak Au...Cl contacts to both $AuCl^-_2$ and $AuCl^-_4$ ions, by which both achieve highly distorted octahedral environments. As the pressure is increased, the Au-Cl...Au units (and hence the octahedra) become more symmetrical; at 5.2 GPa the Cl atoms have moved so far as to render the Au atoms indistinguishable and the structure is that of an Au^{II} complex (see Figure 28).

The structural relationships between several mixed-valence Au halide derivatives have been investigated by Strähle and his co-workers (57, 58, 63). These compounds were $K_2Au_2I_6$ (= $2K^+.AuI^-_2.AuI^-_4$), $Rb_2Au_2Br_6$ (= $2Rb^+.AuBr^-_2.AuBr^-_4$), $Rb_3Au_3Cl_8$ (= $3Rb^+.2AuCl^-_2.AuCl^-_4$) and also $Rb_2AgAu_3I_8$ (= $2Rb^+.Ag^+.2AuI^-_2.AuI^-_4$).

Several mixed-valence compounds mentioned here form black, lustrous crystals. This is typical of metal complexes with interactions between metal centres of formally different oxidation state, and has been interpreted for some of these structures in terms of metal-metal interactions through intervening ligands.

X. Unusual Oxidation States

The 'normal' oxidation states of gold, namely Au^{I} and Au^{III}, are supplemented by a few reported examples of Au^{II} and Au^{V}. In each case one crystal structure supports the assignment of these oxidation states.

Fig. 29 The only known Au^{II} structure (chemical formula given in Figure 19). After (163)

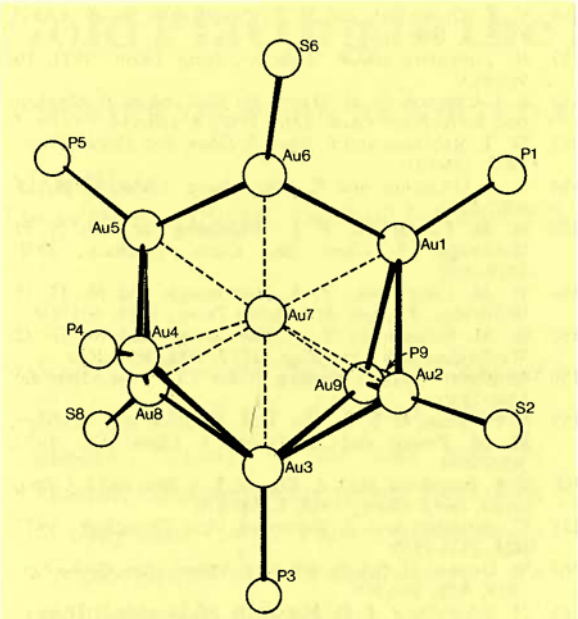

Fig. 30 The newly reported Au_9 cluster. Reproduced from (166) with permission

Au^{II} is represented by the compound shown in Figure 29, prepared from the corresponding Au^{I} heterocycle and one mole of Cl_2. There is an Au-Au bond of 259.7(.5) pm, considerably shorter than in gold clusters, metallic gold or the Au^{I} complexes mentioned in Section IV. It is not clear to what bond order this corresponds. The coordination geometry at each gold atom is approximately square planar (163).

Au^{V} is, as usual for high oxidation states, represented by a fluoride complex. The structure of $[Xe_2F_{11}]^+[AuF_6]^-$ (164nc, 165) confirms the expected octahedral geometry of the AuF_6^- ion, giving the Au-F (average) = 186(1) pm. No F-Au-F angle deviates by more than 2° from ideal values.

Concluding Remarks

The wide range of structures reported here confirms that X-ray crystallography is now established as an essential tool of the chemist. The number of structures published per year continues to grow, and even during the preparation of this article several interesting structures have been established for gold compounds. Those which it has not been possible to discuss fully above contain a new Au_9 cluster as shown in Figure 30 (166); the simple phosphine derivative $(cy_3P)_2Au^+PF_6^-$(166); 'pyAuI', analogous to the chloride, but with linear, rather than zigzag Au...Au linkages (167); and a new phosphorus ylid complex of Au^{I}, the chemical formula of which is included in Figure 19 (52a).

The ease with which crystal structures may nowadays be determined has its drawbacks; there is a tendency (and a pressure) to publish rapidly, often leading to inadequate discussion or, more frequently, to errors in lists of atom coordinates. Nevertheless it may be safely predicted that our knowledge of gold chemistry will continue to be enlarged and enriched by crystallographic results.

Note Added in Proof

Such is the growing interest in gold cluster compounds that three more structures have appeared in time for inclusion in this review. The zerovalent compound $(Ph_3P)Au\text{-}Au(PPh_3)$ has been mentioned briefly (D. M. P. Mingos, *Pure & Appl. Chem.*, 1980, **52**, 705-712); the Au-Au bond is 276 pm long, and the molecule is bent at the Au atoms (no angle given). This is a limiting case of a 'cluster', with just one Au-Au bond. At the other end of the scale of complexity is the cluster $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{2+}$ (C. E. Briant, B. R. C. Theobald, J. W. White, L. K. Bell, D. M. P. Mingos and A. J. Welch, *J. Chem. Soc. Chem. Commun.*, 1981, 201-202), in which the gold atoms form a centred icosahedron; this can be regarded as a 'parent' compound for several other clusters, as discussed above. The first gold cluster with monodentate bridging ligands is $[Au_4I_2(PPh_3)_4]$(F. Demartin, M. Manassero, L. Naldini, R. Ruggeri and M. Sansoni, *J. Chem. Soc. Chem. Commun.*, 1981, 222-223); the gold atoms form a tetrahedron, with iodides bridging two opposite edges.

References

98 E. G. Cox and K. C. Webster, *J. Chem. Soc.*, 1936, 1635-1637
99 R. F. Phillips and H. M. Powell, *Proc. R. Soc. London (A)*, 1939, **173**, 147-159
100 A. Burawoy, C. S. Gibson, G. C. Hampson and H. M. Powell, *J. Chem. Soc.*, 1937, 1690-1693
101 M. F. Perutz and O. Weisz, *J. Chem. Soc.*, 1944, 438-442
102 M. Bonamico and G. Dessy, *Acta Crystallogr.*, 1973, **B29**, 1735-1736
103 M. Bonamico, G. Dessy and A. Vaciago, *Atti Accad. Naz. Lincei, Rend. Cl. Sci. Fis. Mater. Nat.*, 1966, **39**, 504-509
103a J. Strähle and H. Bärnigshausen, *Z. Naturforsch.*, 1970, **25b**, 1186-1187
104 M. Bonamico and G. Dessy, *Acta Crystallogr.*, 1973, **B29**, 1737-1739
105 J. C. Bowles and D. Hall, *Acta Crystallogr.*, 1975, **B31**, 2149-2150
106 P. G. Jones, J. J. Guy and G. M. Sheldrick, *Acta Crystallogr.*, 1975, **B31**, 2687-2688
107 M. R. Caira, L. R. Nassimbeni and A. L. Rodgers, *Acta Crystallogr.*, 1975, **B31**, 1112-1115
108 L. E. Pope and J. C. A. Boeyens, *J. Cryst. Mol. Struct.*, 1975, **5**, 47-58
109 M. S. Hussain and E. O. Schlemper, *J. Chem. Soc. Dalton Trans.*, 1980, 750-755
110 P. G. Jones and G. M. Sheldrick, *Acta Crystallogr.*, 1978, **B34**, 1353-1355
111 J. M. Williams and S. W. Peterson, *J. Am. Chem. Soc.*, 1969, **91**, 776-777
112 A. J. Edwards and G. R. Jones, *J. Chem. Soc. A*, 1969, 1936-1938
113 J. Strähle and H. Bärnigshausen, *Z. Kristallogr.*, 1971, **134**, 471-472
114 R. A. Penneman and R. R. Ryan, *Acta Crystallogr.*, 1972, **B28**, 1629-1632
115 C. Bertinotti and A. Bertinotti, *Acta Crystallogr.*, 1970, **B26**, 422-428
116 C. Bertinotti and A. Bertinotti, *C. R. Acad. Sci.*, 1968, **B267**, 1227-1229
117 C. Bertinotti and A. Bertinotti, *C. R. Acad. Sci.*, 1971, **B273**, 33-36
118 C. D. Gardner and S. C. Wallwork, *J. Chem. Soc. A*, 1970, 3092-3095
119 W. P. Fehlhammer and L. F. Dahl, *J. Am. Chem. Soc.*, 1972, **94**, 3370-3377
120 M. Weishaupt and J. Strähle, *Z. Naturforsch.*, 1976, **31b**, 554-557
121 J. Strähle, private communication

122 H.-D. Wasel-Nielen and R. Hoppe, *Z. anorg. allg. Chem.*, 1970, **375**, 43-54
123 H. Klassen and R. Hoppe, *Naturwissenschaften*, 1976, **63**, 387
124 C. E. Glass, J. H. Konnert, M. G. Miles, D. Britton and R. S. Tobias, *J. Am. Chem. Soc.*, 1968, **90**, 1131-1138
125 M. Peteau-Boisdenghien, J. Meunier-Piret and M. van Meerssche, *Cryst. Struct. Commun.*, 1975, **4**, 375-381
126 S. Komiya, J. C. Huffman and J. K. Kochi, *Inorg. Chem.*, 1977, **16**, 2138-2140
127 D. B. Dell'Amico, F. Calderazzo, F. Marchetti and S. Merlino, *Gazz. Chim. Ital.*, 1978, **108**, 627-633
128 A. Dunand and R. Gerdil, *Acta Crystallogr.*, 1975, **B31**, 370-374
129 G. Nardin, L. Randaccio, G. Annibale, G. Natile and B. Pitteri, *J. Chem. Soc. Dalton Trans.*, 1980, 220-223
130 S. Komiya, J. C. Huffman and J. K. Kochi, *Inorg. Chem.*, 1977, **16**, 1253-1255
131 M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchcock, R. Mason, G. B. Robertson and A. D. C. Towl, *J. Am. Chem. Soc.*, 1971, **93**, 4591-4592
132 M. McPartlin and A. J. Markwell, *J. Organomet. Chem.*, 1973, **57**, C25-C26
133 R. W. Baker and P. Pauling, *J. Chem. Soc. Chem. Commun.*, 1969, 745
134 J. P. Fackler Jr. and C. Paparizos, *J. Am. Chem. Soc.*, 1977, **99**, 2363-2364
135 C. Krüger, J. C. Sekutowski, R. Goddard, H. J. Füller, O. Gasser and H. Schmidbaur, *Isr. J. Chem.*, 1977, **15**, 149-152
136 H. Schmidbaur, G. Müller, K. C. Dash and B. Milewski-Mahrla, *Chem. Ber.*, 1981, **114**, 441-446
137 L. Manojlović-Muir, *J. Organomet. Chem.*, 1974, **73**, C45-C46
138 G. Bandoli, D. A. Clemente, G. Marangoni and L. Cattalini, *J. Chem. Soc. Dalton Trans.*, 1973, 886-889
139 N. W. Alcock, K. P. Ang, K. F. Mok and S. F. Tan, *Acta Crystallogr.*, 1978, **B34**, 3364-3366
140 J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2636-2642
141 J. H. Noordik and P. T. Beurskens, *J. Cryst. Mol. Struct.*, 1971, **1**, 339-345
142 J. H. Noordik, T. W. Hummelink and J. G. M. van der Linden, *J. Coord. Chem.*, 1973, **2**, 185-191
143 P. T. Beurskens, J. A. Cras and J. G. M. van der Linden, *Inorg. Chem.*, 1970, **9**, 475-479
144 J. A. Cras, J. H. Noordik, P. T. Beurskens and A. M. Verhoeven, *J. Cryst. Mol. Struct.*, 1971, **1**, 155-160
145 J. H. Noordik, *Cryst. Struct. Commun.*, 1973, **2**, 81-84
146 P. T. Beurskens, J. A. Cras and J. J. Steggerda, *Inorg. Chem.*, 1968, **7**, 810-813
147 A. W. Gal, G. Beurskens, J. A. Cras, P. T. Beurskens and J. Willemse, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 157-159
148 F. T. H. M. Wijnhoven, W. P. Bosman, J. Willemse and J. A. Cras, *Recl. J. R. Neth. Chem. Soc.*, 1979, **98**, 492-495
149 H. J. Keller, I. Leichert, G. Uhlmann and J. Weiss, *Chem. Ber.*, 1977, **110**, 1684-1690
150 V. F. Duckworth and N. C. Stephenson, *Inorg. Chem.*, 1969, **8**, 1661-1664
151 R. Timkovich and A. Tulinsky, *Inorg. Chem.*, 1977, **16**, 962-963
152 R. J. Charlton, C. M. Harris, H. Patil and N. C. Stephenson, *Inorg. Nucl. Chem. Lett.*, 1966, **2**, 409-414
153 W. T. Robinson and E. Sinn, *J. Chem. Soc. Dalton Trans.*, 1975, 726-731
154 C. J. O'Connor and E. Sinn, *Inorg. Chem.*, 1978, **17**, 2067-2071
155 H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *J. Chem. Soc. Chem. Commun.*, 1976, 1019-1020
156 H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *J. Chem. Soc. Dalton Trans.*, 1978, 303-309
157 H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *Acta Crystallogr.*, 1977, **B33**, 3604-3607
158 N. Elliott and S. L. Pauling, *J. Am. Chem. Soc.*, 1938, **60**, 1846-1850
159 F. H. Brain, C. S. Gibson, J. A. J. Jarvis, R. F. Phillips, H. M. Powell and A. Tyabji, *J. Chem. Soc.*, 1952, 3686-3694
160 P. T. Beurskens, H. J. A. Blaauw, J. A. Cras and J. J. Steggerda, *Inorg. Chem.*, 1968, **7**, 805-810
161 C. Bertinotti and A. Bertinotti, *Acta Crystallogr.*, 1972, **B28**, 2635-2639
162 W. Denner, H. Schulz and H. d'Amour, *Acta Crystallogr.*, 1979, **A35**, 360-365
163 H. Schmidbaur, J. R. Mandl, A. Frank and G. Huttner, *Chem. Ber.*, 1976, **109**, 466-472
164 K. Leary, A. Zalkin and N. Bartlett, *J. Chem. Soc. Chem. Commun.*, 1973, 131-132
165 K. Leary, A. Zalkin and N. Bartlett, *Inorg. Chem.*, 1974, **14**, 775-779
166 M. K. Cooper, G. R. Dennis, K. Henrick and M. McPartlin, *Inorg. Chim. Acta*, 1980, **45**, L151-L152
167 W. Hiller and J. Strähle, private communication

Errata

in Part I of this review (*Gold Bull.*, 1981, **14**, (3), 102-118)

Section III, p. 106: the M-Au-M example should read $[Au\{Co(CO_4)\}_2]^-$

Section IV, p. 109: the *cis*-ethylenic derivative should read $[(Ph_3PAu)C(CF_3)]_2$

Figure 19, a, p. 111: this compound is in fact a 10-membered, not an 8-membered ring

Table III, p. 112: the *p*-tolyl trimer should read $[(ArN{=}COEt)]_3Au$